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EXPERIMENTAL ASSESSMENT OF NITROGEN OXIDES TRANSFORMATIONS WHILE--ETC(U)

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EXPERIMENTAL ASSESSMENT OF NITROGEN OXIDES TRANSFORMATIONS  
WHILE SAMPLING COMBUSTION PRODUCTS

Ronald Clinton Benson

Interim Scientific Report  
AFOSR 74-2710

Prepared For  
Air Force Office of Scientific Research/NA  
Bolling Air Force Base, D.C. 20332

UCI-ARTR-78-1

January 1978

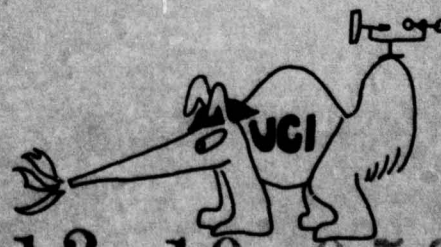
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER <b>AFOSR-TR-79-1232</b>	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) EXPERIMENTAL ASSESSMENT OF NITROGEN OXIDES TRANSFORMATIONS WHILE SAMPLING COMBUSTION PRODUCTS		5. TYPE OF REPORT & PERIOD COVERED <b>9</b> INTERIM <i>scientific rept.</i>	
7. AUTHOR(s) RONALD CLINTON BENSON		6. PERFORMING ORG. REPORT NUMBER <b>14</b> UCI-ARTR-78-1	
9. PERFORMING ORGANIZATION NAME AND ADDRESS UNIVERSITY OF CALIFORNIA, IRVINE UCI COMBUSTION LABORATORY IRVINE, CA 92717		8. CONTRACT OR GRANT NUMBER(s) <b>15</b> AFOSR-74-2710	
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>16</b> 2308A2 61102F <b>17</b> A2	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE <b>11</b> Jan 78	
		13. NUMBER OF PAGES 77	
		15. SECURITY CLASS. (of this report) UNCLASSIFIED	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) COMBUSTION AIR POLLUTION COMBUSTION SAMPLING			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Analysis of combustion products is performed by conveying the exhaust effluents to instrumentation by means of a sample probe and sampling line. Frequently, the selection of sampling materials does not consider potential chemical transformations that can occur in the sample line and probe. Nitrogen oxides are combustion products that are especially vulnerable to transformations. Nitric oxide (NO) and nitrogen dioxide (NO <sub>2</sub> ) are the primary components of NO <sub>x</sub> . The ratio of NO/NO <sub>2</sub> emissions from combustion sources is not well established (due			

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to the potential reduction of  $\text{NO}_2$  to  $\text{NO}$  in sample probes and sample lines) and the total emission of  $\text{NO}_x$  is subject to uncertainty in some cases (due to potential removal of  $\text{NO}_x$  in sample probes and sample lines). The objective of the present study is to investigate the extent of transformations of  $\text{NO}_x$  in the presence of oxidizing and reducing species. Stainless steel and silica were the two sampling tube materials used in this investigation. Simulated combustion products of 500 ppm  $\text{NO}$ , 75 ppm  $\text{NO}_2$ , 12%  $\text{CO}_2$  bal  $\text{N}_2$  at  $25^\circ\text{C}$  were common to all tests. The oxidizing species and concentrations considered included 1 and 5%  $\text{O}_2$ . Various concentrations of carbon monoxide, hydrogen, and hydrocarbons were used for the reducing species. Temperature and pressure effects were evaluated in this particular study. The results indicated that transformation was more pronounced in stainless steel than silica. Reduction of  $\text{NO}_2$  to  $\text{NO}$ , and removal of  $\text{NO}_2$  and  $\text{NO}$  were the dominant transformation types observed. In the presence of reactive reducing species (e.g. hydrogen, propylene, and ethylene), reduction of  $\text{NO}_2$  to  $\text{NO}$  occurred as low as  $200^\circ\text{C}$  in stainless steel, at  $300^\circ\text{C}$  in the presence of hydrogen in silica, and at  $400^\circ\text{C}$  in the presence of ethylene or propylene in silica. Removal of  $\text{NO}_x$  by both hydrogen and propylene was observed in the absence of oxygen at  $300^\circ\text{C}$  in stainless steel, and removal of  $\text{NO}_x$  by ethylene was observed at  $400^\circ\text{C}$ . In the presence of less reactive reducing species (e.g. methane and carbon monoxide), either higher concentrations or higher temperatures were required to reduce  $\text{NO}_2$  to  $\text{NO}$ . The presence of oxygen suppressed but did not prevent the reduction of  $\text{NO}_2$  to  $\text{NO}$ . Neither methane nor carbon monoxide were active in removing  $\text{NO}_x$ . The present data were collected in the pressure range of 1.0 and 1.15 atmospheres.

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## Chapter 1

### INTRODUCTION

The analysis of exhaust gases from anthropogenic sources such as the spark ignited internal combustion engine, compression ignited diesel engines, gas turbine engines, power plants, and package boilers is critical in terms of monitoring pollutant emission levels and measuring operating efficiency. In order to undertake an accurate assessment of pollutant emissions, a sampling line and probe are needed to convey the gases from the exhaust plane of the combustion source to analytical instruments for subsequent analysis. Figure 1-1 illustrates schematically a typical sampling train. An important criterion for selecting a sampling train is to maintain the integrity of the chemical species between the point of measurement and the analytical instrumentation. Any significant chemical transformations occurring within the sampling line will compromise emission measurements.

Of all the significant products of combustion, oxides of nitrogen ( $\text{NO}_x$ ) are especially susceptible to chemical transformations. The species of primary interest in the oxides of nitrogen family are nitric oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ). The present study was undertaken to experimentally assess the extent to which and conditions under which nitrogen oxides experience chemical change when sampling.

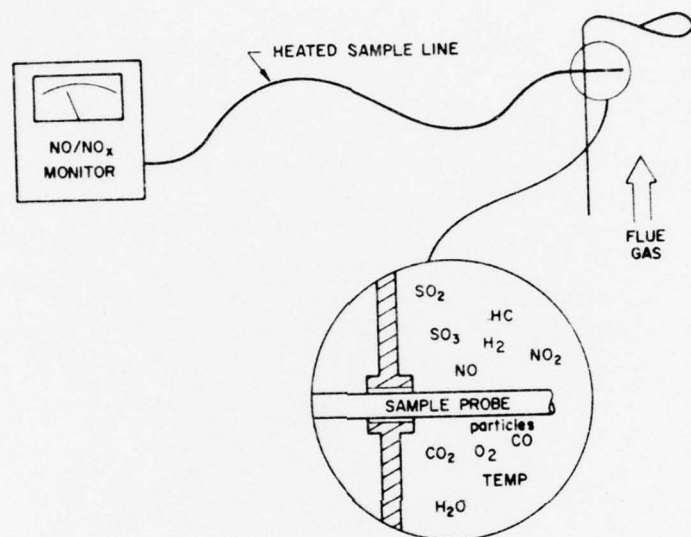


FIGURE 1-1 COMBUSTION PRODUCT SAMPLING TRAIN

## 1.1 NO<sub>x</sub> EMISSIONS

The variety of combustion sources from which oxides of nitrogen are emitted is presented in Table 1-1. A broad range of effluent concentrations, mixture ratios, and sampling temperatures are identified for a number of combustion systems.

The amount of NO<sub>x</sub> measured from a combustion source will depend on the combustion device, fuel, and fuel/air mixture ratio. For any combustion process, the stoichiometric or chemically correct fuel/air mixture ratio is the amount of fuel/air by mass required for complete combustion. The products of complete combustion consist of carbon dioxide (CO<sub>2</sub>), water vapor (H<sub>2</sub>O), and nitrogen (N<sub>2</sub>). However, most combustion processes are incomplete and/or operate with excess air. As a result, the combustion products coexist in either an oxidizing or reducing environment. For oxidizing environments, the oxygen available is sufficient to oxidize the remaining reducing species (e.g. CO, H<sub>2</sub>, HC's) given enough time. For reducing environments the available oxygen, if any, is not sufficient to fully oxidize the reducing species remaining regardless of the time available.

The electric generating steam boiler is a good example of a combustion source that operates in an oxidizing environment. The operating conditions of the boiler are conducive to oxidizing hydrocarbons and carbon monoxide.



Table 1-1 Sampling conditions for nitrogen oxides.

Source	Typical NO <sub>x</sub> ppm	Sampling Point	Typical Sampling Environment Temperature °C	Examples of NO <sub>x</sub> Probing	References Prior Studies Relevant to NO <sub>x</sub> Changes
Internal Combustion Engine	500-4000	Combustion Zone	1300-2400	Zuonow et al. 1967 Alperstein and Bradow 1965	- - - - -
	500-1000	Engine Exhaust	200-500	EPA 1974a EPA 1975	Halstead et al. 1972
Diesel Engine	1000-7000	Combustion Zone	700-2500	Bennethum et al. 1975	- - - - -
	700-2500	Engine Exhaust	200-500	EPA 1974b	Halstead et al. 1972
Residential Oil Burners	20-100	Flue Gas	100-300	Barrett 1973	Halstead et al. 1972
Boilers	200-1000	Combustion Zone	100-1600	Muzio and Wilson 1973 Kruswiede et al. 1975	England et al. 1973 Schefer et al. 1973 Allen 1975
	25-800	Flue Gas	100-300	EPA 1976 Bartok et al. 1971 Cato and Robinson 1974	Halstead et al. 1972
Gas Turbine	1000-8000	Combustion Zone	1300-2700	Tuttle et al. 1973	- - - - -
	25-200	Engine Exhaust	400-1500	Pew et al. 1977 Davidson and Domal 1972 Blasowski and Henderson 1972 Elwood and Dieck 1974 Grossman et al. 1974	Tuttle et al. 1973 Halstead et al. 1972
Flame Research	10-8000	Within Flame	700-2500	Cernaneky and Sawyer 1975 Merryman and Levy 1975 Penimore 1971 Penimore 1975 Pompei and Heywood 1972 Malte and Pratt 1973	England et al. 1973 Schefer et al. 1973 Allen 1975

The amount of excess air and sufficient residence times at maintained temperatures enable virtually complete oxidation of reducing species to occur. Flue gas emissions of  $\text{NO}_x$  from boilers will typically vary from 25-800 ppm at temperatures of 100-300°C.

The automobile is typical of combustion sources operating in a reducing environment. Incomplete combustion under actual operating conditions produces carbon monoxide (CO), hydrocarbons (HC's), particulates and hydrogen ( $\text{H}_2$ ) in addition to nitrogen oxides ( $\text{NO}_x$ ). Engine exhaust emissions of  $\text{NO}_x$  from automobiles will typically vary from 500-1000 ppm at temperatures of 200-500°C.

Although  $\text{NO}_x$  sampling of flue gases from automobiles and boilers involves moderate temperatures (25-600°C), sampling temperatures do vary widely in flame and combustion research. Three major temperature groups have been identified for  $\text{NO}_x$  sampling (Samuelsen and Harman, 1975):

<u>Temperature Group</u>	<u>Temperature Range</u>
moderate	25-600°C
high	600-1200°C
very high	1200-2500°C

The moderate temperature range is most frequently found in sampling flue gases from mobile sources (e.g. the automobile) and stationary sources (e.g. package boilers).

High temperature probing occurs in combustion research while very high temperature probing is common in flame research. Although flame research has historically been conducted in laboratory systems (premixed flames, diffusion flames, shock tubes, stirred reactors and plug flow reactors) combustion zones in practical combustion systems are now being probed as well (Muzio and Wilson, 1973 and Krumweide et al., 1975).

## 1.2 MEASUREMENT OF $\text{NO}_x$

Measurement of total  $\text{NO}_x$  emissions from flames and combustors are compromised by  $\text{NO}_x$  removal in sample lines and probes.  $\text{NO}_x$  are reactive combustion products, and precaution must be employed to avoid removal. General reviews of  $\text{NO}_x$  sampling problems are available to assist in designing sampling systems (Halstead and Munro, 1971; Halstead, 1971; Tuttle et al., 1973; Allen, 1973; and Allen et al., 1974). Additional information is available from specialized combustion studies (Halstead et al., 1972; England et al., 1973; Schefer et al., 1973; and Allen, 1975), chemiluminescent analyzer converter studies (Hodgeson et al., 1971; Sigsby et al., 1973; and Breitenbach and Shelef, 1973), studies conducted to explore the catalytic oxidation of CO in automobile exhaust by  $\text{O}_2$  and NO (Baker and Doerr, 1965; Shelef et al., 1968; and Ayen and Ng, 1966).

In addition to the measurement of total  $\text{NO}_x$ , the determination of the  $\text{NO}/\text{NO}_2$  ratio is becoming of increasing

interest. Although the  $\text{NO}/\text{NO}_2$  ratio from combustion sources is uncertain, typical estimates of 90-95% NO and 5-10%  $\text{NO}_2$  have been made in the literature (e.g. Seinfeld, 1975). The emission standards, currently proposed or promulgated by the Environmental Protection Agency (EPA), limit the emission of  $\text{NO}_x$  but do not, as yet, address the relative amounts of NO and  $\text{NO}_2$  allowed. Current emission inventories specify NO and  $\text{NO}_2$  in terms of total  $\text{NO}_x$  for both mobile sources (e.g. the automobile) and stationary sources (e.g. power plants). The significance of the  $\text{NO}/\text{NO}_2$  ratio has been reported by Samuelsen and Harman (1975) for a number of applications:

- (1) Assessment of local air quality impact due to nitrogen dioxide ( $\text{NO}_2$ ) emissions from line sources (e.g. roadways and highways) requires the determination of the amount of nitrogen dioxide ( $\text{NO}_2$ ) emitted as a primary pollutant.
- (2) Assessment of plume visibility impact from power plants requires the determination of the amount of nitrogen dioxide and nitric oxide emitted as primary pollutants.
- (3) Regional oxidant modeling requires a spatial and temporal geocoded emissions inventory for both nitric oxide and nitrogen dioxide.
- (4) Measurement of the  $\text{NO}/\text{NO}_2$  ratio in flames is required to identify the chemical kinetic mechanisms responsible.



These applications require knowledge of the proportion of nitric oxide to nitrogen dioxide emitted from combustion sources. However, without knowledge of the possible chemical transformations occurring within sampling lines and probes, an accurate assessment of the  $\text{NO}/\text{NO}_2$  ratio cannot be made.

### 1.3 PRESENT STUDY

To more clearly establish the role of probes and sampling lines in  $\text{NO}_x$  transformations, the following objectives were established:

- (1) To examine probe and sampling materials for sampling combustion effluents at moderate temperatures ( $25\text{-}400^\circ\text{C}$ ) in the presence of oxidizing species ( $\text{O}_2$ ) and reducing species ( $\text{CO}$ ,  $\text{H}_2$ , HC's)
- (2) To provide preliminary information regarding sources of error, if any, while using conventional stainless and silica materials for sampling combustion effluents at moderate temperatures ( $25\text{-}400^\circ\text{C}$ ) in the presence of oxidizing and reducing species

To meet the objectives, an experimental system was designed to explore  $\text{NO}_2$  and  $\text{NO}$  transformations in probes and sample lines under controlled laboratory conditions. Concentration changes of  $\text{NO}$  and  $\text{NO}_2$  across isothermally

maintained 2 meter sample tubes were monitored.  $\text{NO}_2$  and NO transformations were investigated for the following conditions:

mixtures: simulated, dry combustion products

$\text{O}_2$ : 0,1,5%  
NO: 500 ppm  
 $\text{NO}_x$ : 575 ppm  
CO: 0,100,1000,2500 ppm  
HC: 0,500,1000 ppm (methane  
ethylene, propylene)  
 $\text{H}_2$ : 0,.5%,3%  
 $\text{CO}_2$ : 12%  
 $\text{N}_2$ : balance

materials: 316 stainless steel, silica

temperature range: 25-400°C

The experimental system was designed to simulate sampling conditions encountered in practice. The concentration of oxidizing and reducing species cover a wide range of combustion effluent levels. The lower concentrations of CO and HC's simulate fuel lean emissions characteristic of the package boiler (Cato et al., 1975) and the gas turbine engine during cruise (Jones et al., 1974). Higher concentrations of CO and HC's with unburned hydrogen are representative of fuel rich emissions from the automobile (Seinfeld, 1975) and the gas turbine engine during idle and taxi (Jones et al., 1974). Methane ( $\text{CH}_4$ ), ethylene

( $C_2H_4$ ) and propylene ( $C_3H_6$ ), the three hydrocarbon species investigated, are all prominent species emitted from the automobile (Olson Labs, 1977; Black and Braden, 1975; and Black, 1976). The NO and NO<sub>2</sub> concentrations simulate those observed in combustion source effluents (Table 1-1). 316 stainless steel and silica glass represent conventional sampling materials. The temperature range (25-400°C) coincides with those temperatures associated with engine exhaust from the automobile and flue gases from boilers (Table 1-1).

## Chapter 2

## BACKGROUND

2.1 NO<sub>x</sub> TRANSFORMATION TYPES

Chemical transformations of nitrogen oxides in sampling lines and probes may be divided into four categories (Samuelsen and Harman, 1977):

NO OXIDATION	$\text{NO} \longrightarrow \text{NO}_2$	NO <sub>x</sub> conserved
NO <sub>2</sub> REDUCTION	$\text{NO}_2 \longrightarrow \text{NO}$	NO <sub>x</sub> conserved
NO <sub>x</sub> REMOVAL	$\text{NO}, \text{NO}_2 \longrightarrow \text{N}_2, \text{NH}_3, \text{HCN} \dots$	NO <sub>x</sub> not conserved
NO <sub>x</sub> FORMATION	$\text{C}_W\text{N}_X\text{H}_Y \longrightarrow \text{NO}, \text{NO}_2$	NO <sub>x</sub> not conserved

The fourth chemical mechanism, formation, involves the oxidation of nitrogen containing species such as ammonia (NH<sub>3</sub>). Formation of nitrogen oxides in probes and sampling lines are generally limited to specialized conditions (e.g. sample extraction from flue gases into which ammonia has been injected for NO<sub>x</sub> control, or from flames into which nitrogen containing compounds have been injected to study fuel bound nitrogen oxides formation).

2.2 INVESTIGATIONS OF NO<sub>x</sub> TRANSFORMATIONS

The following sections review investigations of NO<sub>x</sub> studies pertinent to the experimental study. Studies of catalytic and gas phase reactions with mixtures containing NO and/or NO<sub>2</sub> in the presence of oxygen and reducing species are described. The methods of conventional sampling versus optical techniques are also reported. A summary of the



transformation reactions proposed in the literature to be active in probes and sample lines is presented in Table 2-1. Whether these reactions or others in addition may be active is the object of continuing investigation.

### 2.3.1 OXYGEN( $\text{NO}_2/\text{NO}/\text{O}_2/\text{N}_2$ ) MIXTURES

Investigators have observed catalytic reduction of  $\text{NO}_2$  in the absence of oxygen. White and Beddows (1973) observed that a two meter long 321 stainless steel converter totally reduced an initial mixture of 25 ppm  $\text{NO}_2$ , balance  $\text{N}_2$  at approximately  $200^\circ\text{C}$ .

Furthermore, Halstead (1971) reported that stainless steel probes catalytically reduced  $\text{NO}_2$  at temperatures above  $300^\circ\text{C}$  for a gas concentration of 30 ppm  $\text{NO}_2$ , bal  $\text{N}_2$ . A six foot length of unspecified stainless steel was used for the study.

Catalytic reduction of  $\text{NO}_2$  has also been observed in the presence of oxygen. However, the reduction is less pronounced in the presence of oxygen than in the absence of oxygen. Wikstrom and Nobe (1965) observed that the conversion to  $\text{N}_2$  and  $\text{O}_2$  was less in air than in  $\text{N}_2$  for a  $\text{CuO}$ -alumina catalyst. For the initial  $\text{NO}_2$  concentration (1260 ppm) and temperature range ( $304$ - $520^\circ\text{C}$ ), 55% conversion of  $\text{NO}_x$  in  $\text{N}_2$  was observed compared to 47% conversion of  $\text{NO}_x$  in air.

Oxygen may not only inhibit catalytic reduction of

Table 2-1 Homogeneous, Heterogeneous, and Catalytic NO<sub>x</sub> Reactions

Transformation (Reaction Type)	Reaction	Temp(°C)	Study	Reference
<b>NO OXIDATION</b>				
Homogeneous	$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	25	Gas Phase	Halstead and Munro (1971)
Heterogeneous	$\text{NO} + \text{O} \xrightarrow{\text{wall}} \text{NO}_2$	- - -	Flame	Allen (1975)
Catalyst	$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	- - -	Combustion	Halstead and Munro (1971)
	$\text{Cr}_2\text{O}_3 + \text{NO} \rightarrow 2\text{CrO}_2 + \text{NO}_2$	400-600	Combustion	Hilliard and Wheeler (1977)
<b>NO<sub>2</sub> REDUCTION</b>				
Homogeneous	$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	130-620	Gas Phase	Latimer and Hildebrand (1964)
	$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$	- - -	Flame	Allen (1975)
	$\text{H}_2 + \text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}$	400	Gas Phase	Ashmore and Levitt (1956, 1957)
	$\text{CH}_4 + \text{NO}_2 \rightarrow \text{CO}, \text{CO}_2, \text{CH}_4, \dots$	350-400	Gas Phase	Bromberg and Taylor (1955)
	$\text{CO}, \text{CO}_2, \text{NO}, \dots$	300-400	Gas Phase	Gagarina and Emanuel (1959)
Heterogeneous	$\text{NO}_2 + \text{metal} \rightarrow \text{metal oxide} + \text{NO}$ wall	25-400	Combustion	White and Beddows (1973)
	$\text{NO}_2 + \text{C} \xrightarrow{\text{wall}} \text{CO} + \text{NO}$	400 750	Converter Converter	Breitenbach and Shelef (1973) Breitenbach and Shelef (1973)
Catalyst	$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	300	Combustion	Halstead (1971)
		475-750	Converter	Breitenbach and Shelef (1973)
		25-600	Converter	Hodgeson et al. (1971)
		750	Converter	Sigsby et al. (1973)
		200-400	Combustion	White and Beddows (1973)
		304-520	Catalyst	Wikstrom and Nobe (1965)
	$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$	180-250	Catalyst	Ayen and Yonebayashi (1967)
	$\text{NO}_2 + \text{CO} \rightarrow \text{products}$	25-400	Combustion	White and Beddows (1973)
	$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	304-520	Catalyst	Wikstrom and Nobe (1965)
<b>NO<sub>x</sub> REMOVAL</b>				
Homogeneous	$\text{NO} + \text{HC} \rightarrow \text{CHO} + \text{N}$	823-1423	Gas Phase	Myerson and Blair (1975) Myerson (1975)
Heterogeneous	$\text{NO}_2 + \text{wall} \rightarrow \text{absorbed}$ adsorbed	- - -	Combustion	Halstead and Munro (1971) Allen (1975) Halstead et al. (1972)
	$\text{NO}(\text{NO}_2) + \text{metal} \rightarrow \text{metal oxide} + \text{N}_2$ wall	500-750	Converter	Siewert (1975)
	$\text{NO}_2 \xrightarrow{\text{condensate}} \text{absorbed}$	- - -	Combustion	Allen (1975) McNulty (1974)
Catalyst	$\text{NO} + \text{CO} \rightarrow \text{CO}_2 + 1/2\text{N}_2$	25-1700	Combustion	Halstead et al. (1972)
		100-600	Catalyst	Shelef et al. (1968)
		160-240	Catalyst	Ayen and Ng (1965)
		115-270	Catalyst	Baker and Doerr (1972)
		320-510	Catalyst	Shelef and Gandhi (1972)
	$\text{H}_2 + \text{NO} \rightarrow \text{NH}_3, \dots$	100-750	Catalyst	Shelef and Gandhi (1972)
	$5\text{H}_2 + \text{NO} \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$	370-600	Catalyst	Klimisch and Barnes (1972)
		347-502	Catalyst	Lamb and Tolleson (1975)
		375-425	Catalyst	Ayen and Peters (1962)
	$\text{NO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + 1/2\text{N}_2$	375-425	Catalyst	Ayen and Peters (1962)
	$2\text{NO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}$	150-300	Catalyst	Peterson et al. (1972)
	$\text{NO} + \text{H}_2 \rightarrow \text{N}_2 + \text{products}$	480	Catalyst	Peterson et al. (1972)
	$\text{C}_3\text{H}_6 + \text{NO} \rightarrow \text{NH}_3, \dots$	420-550	Catalyst	Shelef and Gandhi (1974)
	$\text{C}_3\text{H}_6 + \text{NO} \rightarrow 2\text{HCN} + 3\text{H}_2\text{O} + 1/2\text{N}_2$	520	Catalyst	Germain (1969)

$\text{NO}_2$  but also promote the oxidation of  $\text{NO}$  to  $\text{NO}_2$ . Hilliard and Wheeler (1977) observed that for mixtures of 1000 ppm  $\text{NO}$ , 5%  $\text{O}_2$ , bal  $\text{N}_2$ , oxidation of  $\text{NO}$  to  $\text{NO}_2$  was observed at temperatures of  $400^\circ\text{C}$  to  $600^\circ\text{C}$  in 316 stainless steel. The results were attributed to the activation of the chromium oxide transition at  $400^\circ\text{C}$ .

### 2.3.2 CARBON MONOXIDE( $\text{NO}_2/\text{NO}/\text{O}_2/\text{N}_2/\text{CO}$ ) MIXTURES

Several investigators (Baker and Doerr, 1965; Shelef et al., 1968; and Ayeen and Ng, 1966) have explored the catalytic oxidation of  $\text{CO}$  in automobile exhaust by  $\text{O}_2$  and  $\text{NO}$ . Oxygen was observed to preferentially oxidize  $\text{CO}$  to  $\text{CO}_2$  at  $500^\circ\text{C}$  for a number of catalysts. Furthermore, Stricker and Meinel (1977) observed that a stainless steel converter operating between  $500^\circ\text{C}$  and  $700^\circ\text{C}$  promotes the oxidation of  $\text{CO}$  to  $\text{CO}_2$  by residual oxygen present in the exhaust gas from a spark-ignition engine. Experimental data obtained by Hilliard and Wheeler (1977) supported the oxidation of  $\text{NO}$  to  $\text{NO}_2$  by the chromium content in 316 stainless steel. Carbon monoxide inhibited the  $\text{NO}$  oxidation but only at  $\text{CO}$  concentrations above 1000 ppm. The catalytic activity of stainless steel while sampling  $\text{NO}_x$  and  $\text{CO}$  from combustion systems has also been investigated by Halstead et al. (1972) and White and Beddows (1973).

The work by Halstead et al. (1972) is the most definitive regarding potential transformations of nitrogen

oxides in the presence of carbon monoxide while sampling combustion products. Actual combustion products from a Tunnel Mixing Burner were sampled under both lean and fuel rich conditions. A supply of natural gas with air was used as the burning mixture. Stainless steel and silica were the two probe materials evaluated (stainless steel 210 cm long by 6 mm i.d. and silica tubing, 210 cm long by 6 mm i.d.). The temperature at the probe inlet varied between 800 and 1700°C and the probe outlet temperature was about ambient.

Halstead observed no change in  $\text{NO}_x$  readings between silica and stainless steel probes under lean fire conditions. Conflicting readings were observed between the stainless and silica probes under rich fire conditions.  $\text{NO}_x$  was removed in excess of 90% in the stainless steel probe while no  $\text{NO}_x$  removal was observed in the silica probe. Halstead's work demonstrated that reducing atmospheres in the presence of stainless steel probes affect  $\text{NO}_x$  readings. The unknown concentrations of reducing species (e.g.  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{HC}$ 's) at which the reduction and removal reactions occur and temperature gradient along the probe length prevent assessment of the conditions for activation of the reduction and removal mechanism.

White and Beddows (1973) investigated  $\text{NO}_2$  reduction by  $\text{CO}$  in a 321 stainless steel sampling line. The initial gas mixture consisted of 25 ppm  $\text{NO}_2$  and 450 ppm  $\text{CO}$  bal  $\text{N}_2$ . The loss of  $\text{NO}_2$  was more pronounced in the presence



of CO than in its absence.

### 2.3.3 HYDROGEN ( $\text{NO}_2/\text{NO}/\text{O}_2/\text{N}_2/\text{CO}/\text{H}_2$ ) MIXTURES

Reactions between NO and  $\text{NO}_2$  and hydrogen have been studied in both gas phase and catalytic investigations. Ashmore and Levitt (1956,1957) observed the reduction of  $\text{NO}_2$  by  $\text{H}_2$  to be essentially homogeneous with high  $\text{H}_2$  to  $\text{NO}_2$  ratios at approximately  $400^\circ\text{C}$ .

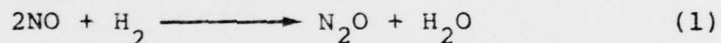
Several investigators have explored the catalytic reduction of NO by  $\text{H}_2$  at temperatures between  $200^\circ\text{C}$  and  $500^\circ\text{C}$ . Lamb and Tolleson (1975) observed that a solid alloy monel catalyst, containing copper and nickel, is effective for the reduction of NO by hydrogen in high velocity gas streams containing low concentrations of NO and  $\text{O}_2$ . The  $\text{H}_2$  concentration ranged from .06-2.50% and the NO concentration ranged from .22-.31%. Specifically, the proportion of NO removed increased with decreasing inlet oxygen and increasing hydrogen partial pressures at temperatures above  $350^\circ\text{C}$ .

Klimisch and Barnes (1972) reported that gases containing hydrogen or compounds producing hydrogen can reduce nitric oxide in the presence of  $\text{Cr}_2\text{O}_3$  or copper oxide catalysts at temperatures of  $375^\circ\text{C}$ .

Shelef and Gandhi (1972) investigated the role of general catalysts in ammonia formation from a mixture of nitric oxide and molecular hydrogen. The temperature for

90% NO conversion was determined in NO-H<sub>2</sub>, NO-H<sub>2</sub>-CO, and NO-CO systems with copper chromite, copper oxide, nickel oxide, and iron oxide catalysts. The inlet gas composition consisted of 1000-1200 ppm NO, 1.4% H<sub>2</sub> and 1.4% CO. The catalyst temperatures ranged from 210-510°C. All catalysts examined except nickel oxide and iron oxide showed higher conversion of NO with H<sub>2</sub> than with CO. The effect of NO with a H<sub>2</sub> and CO mixture was a higher conversion than with either reducing species singularly.

Peterson, Landau, and Saucedo (1974) observed nitrous oxide as a product of the nitric oxide-hydrogen reaction on a stainless steel catalyst at 340°C:



N<sub>2</sub>O was measured as a gas intermediate at moderate temperatures (150-300°C) and was not present at higher temperatures in most heterogeneous catalytic reactions of NO on a reduced stainless steel surface. At higher temperatures, the reaction of nitric oxide and hydrogen formed N<sub>2</sub> and other products.

Further studies by Ayen and Peters (1962) validated the importance of more than one reaction from the catalytic interaction between hydrogen and nitric oxide. Reduction to N<sub>2</sub> or NH<sub>3</sub> was observed for the stainless steel flow reactor used.

The investigations reported show that hydrogen can

reduce nitric oxides over a number of catalytic surfaces for a temperature range of 200-500°C. The products depend on the reaction temperature. Hydrogen appears to be more reactive with NO than CO for most catalysts.

#### 2.3.4 HYDROCARBON (NO<sub>2</sub>/NO/O<sub>2</sub>/N<sub>2</sub>/HC) MIXTURES

The reaction of hydrocarbons with nitrogen oxides has been observed for both catalytic and homogeneous conditions. Shelef and Gandhi (1972) examined ammonia formation (NH<sub>3</sub>) from the reaction of NO and hydrocarbons in the absence of oxygen on a number of catalysts. The absence of ammonia formed from hydrogen with paraffins was associated with the low hydrogen saturation of the surface. Olefins were noted to react more readily with NO and even under dry conditions some NH<sub>3</sub> formation was observed in catalytic interaction.

Roth and Doerr (1961) observed that hydrocarbon oxidation in the presence of NO and O<sub>2</sub> is appreciable at temperatures above 250°C with a chromite catalyst. The amount of oxygen added was 4% and space velocity was 10000 hr<sup>-1</sup>.

Myerson (1975) and Myerson and Blair (1976) have observed homogeneous gas phase removal of NO in the presence of hydrocarbons at elevated temperatures (1100-1700°K) including gas phase removal of NO in automobile exhaust. Dimitriadis (1967) associated observed losses of NO<sub>2</sub> to

hydrocarbon exhaust products of the automobile. The extent of  $\text{NO}_2$  removal was dependent on the type of fuel being used as well as the engine conditions. However, the type of fuel affecting the extent of the  $\text{NO}_2$ -hydrocarbon reaction could not be indicated. Fuels included indolene, isooctane, olefin rich fuel, and aromatic rich fuel.

The gas phase reduction of  $\text{NO}_2$  by methane has been studied by a number of investigators. Bromberg and Taylor (1955) studied the reaction in a static system ( $350\text{--}400^\circ\text{C}$ ) in a cylindrically fused silica reactor and observed that the principal products were  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and unreacted  $\text{CH}_4$  for residence times of approximately one minute. Studies conducted by Gagarina and Emanuel (1959) identified  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}$ , and traces of nitromethane, formaldehyde and  $\text{HCN}$  as products of the methane-nitrogen dioxide reaction in a cylinder of molybdenum glass. The sampling times ranged from 0-30 minutes.

#### 2.4 STAINLESS VS. SILICA PROBES

The levels of  $\text{NO}$  and  $\text{NO}_2$  while sampling from a stainless steel and silica probe have been shown to depend on equivalence ratio. England et al. (1973) observed  $\text{NO}$  measurements from a flue gas with a 321 SS probe were considerably less than in near stoichiometric and fuel rich methane air flames. At equivalence ratios of .7 or less (fuel lean), no difference in  $\text{NO}$  measurements was detected



between a 321 stainless steel tube and a quartz tube. Halstead et al. (1972) also observed conflicting readings between stainless steel and silica probes under rich fire conditions.  $\text{NO}_x$  was removed in excess of 90% in the stainless probe while no  $\text{NO}_x$  removal was observed in the silica probe.

Under certain conditions, quartz probes have been observed to significantly transform oxides of nitrogen. Cernansky (1974) reported that measurements using hydrogen fuel in a laboratory diffusion flame resulted in the aging of probes. The surfaces of both quartz and stainless cooled probes were reduced by the hydrogen gas such that NO and  $\text{NO}_2$  decreased with time. Water cooling has been shown to be a necessity in quartz probes to prevent significant reduction of NO (England et al., 1973) and formation of NO (Cernansky, 1976). However, Allen et al. (1974) found for temperatures less than  $750^\circ\text{C}$  no evidence of NO or  $\text{NO}_2$  loss was observed while sampling with uncooled silica probes.

The probability of NO removal from sampling probes and lines used in practice has been reinforced by employing optical techniques. Few, Bryson, and McGregor (1977) have examined NO measurement at the exhaust plane of a gas turbine combustor using conventional methods and optical techniques. Conventional probing measured NO concentrations by a factor of three to six fold lower than optical

measurements.

## 2.5 SUMMARY

Although the evidence of  $\text{NO}_x$  transformations in the presence of oxidizing and reducing species is supported by several investigations, key questions pertinent to the present study still remain. A systematic, controlled experiment simulating the probe and sampling environment has been designed to assess the conditions and the extent to which oxides of nitrogen experience change while sampling. The following questions are addressed:

- (1) What concentrations of oxidizing and reducing species promote the transformation of NO and  $\text{NO}_2$ ?
- (2) At what temperature is transformation promoted?
- (3) How does the effect differ between probe and sample line materials of interest, namely 316 stainless steel and silica quartz?

To assess these questions, an experimental system was designed to explore the transformation of nitrogen oxides.

## Chapter 3

## EXPERIMENT

The experimental study was designed to assess NO and NO<sub>2</sub> transformations that may be encountered from combustion devices that operate fuel rich (e.g. automobile engines) and air rich (e.g. boilers, diesel engines, and gas turbine engines). A schematic of the experimental system is shown in Figure 3-1. Test parameters included carrier gas composition, concentration and composition of the dopant gases, temperature, pressure, and sample tube material. The combustion products were simulated to control maintenance of the inlet composition of the carrier gas and dopant gases.

High concentration cylinder sources of doping gases (NO, NO<sub>2</sub>, CO, H<sub>2</sub>, and HC's) were diluted by a carrier gas (0,1, or 5%O<sub>2</sub>, 12%CO<sub>2</sub>, bal N<sub>2</sub>) to simulate primary combustion products. The rationale for selecting the carrier gas is specified quantitatively by the stoichiometric mixture of methane gas with air:

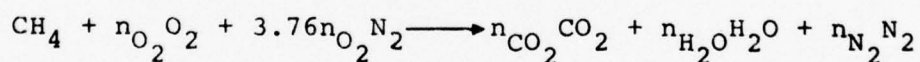


Table 3-1 shows the percent composition of exhaust products by volume on both a dry and wet basis. Since the exhaust gas simulation was performed without introducing water (H<sub>2</sub>O) to the system, a typical dry basis composition of 12%CO<sub>2</sub>, 0,1, or 5%O<sub>2</sub>, bal N<sub>2</sub> was selected. Porous sintered flow restrictors were utilized to control the doping gas

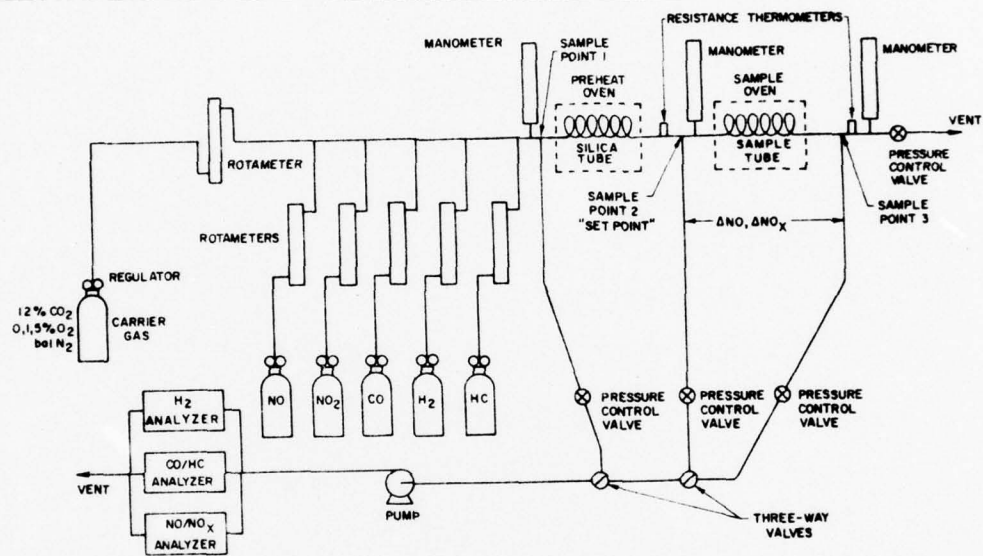


FIGURE 3-1 EXPERIMENTAL SYSTEM



Table 3-1

## STOICHIOMETRIC COMBUSTION OF METHANE-AIR (VOLUME BASIS)

	$\frac{\text{CO}_2}{2}$	$\frac{\text{H}_2\text{O}}{2}$	$\frac{\text{N}_2}{2}$
Dry Basis	11.7%	---	88.3%
Wet Basis	9.4%	19.1%	71.5%

flowrates. The carrier gas flowrate was maintained at 4.0 liters/minute (STP). A pyrex glass manifold was designed to enable sufficient mixing of the carrier gas with the doping gases. After doping the carrier gas entered a silica preheat oven to raise the temperature of the gas to the test temperature. A test oven maintained the gas temperature constant thru the sample tube.

Sample tube materials evaluated in the present study included 2 meter lengths of 6.4 mm (0.250 inch) O.D., 4.0 mm (0.180 inch) I.D., 316 stainless steel and silica glass (Vycor, Corning Glass Works). The gas temperature was incrementally increased from 25°C to 400°C. Temperatures of the gas stream ( $T_2$  and  $T_3$ ) were measured with insulated platinum resistance thermometers centered in the probe bore at the inlet and outlet of the sample tube. The space velocity in the sample tube ranged from 7600 hr<sup>-1</sup> (25°C) to 19500 hr<sup>-1</sup> (400°C) for the 4.0 liter/minute inlet volumetric flowrate selected for the present study. Table 3-2 shows the variation of residence time and space velocity with temperature and probe material.

Table 3-3 presents the test matrix used in the experiment. The NO and NO<sub>2</sub> input levels to the sample tube (Sample Point 2) were chosen to be 500 ppm and 75 ppm respectively. Gas composition was measured at Points 2 & 3 to assess the extent of NO and NO<sub>2</sub> concentration change within the 2 meter sample tube. Gas composition was also

Table 3-2  
RESIDENCE TIME AND SPACE VELOCITY VERSUS  
TEMPERATURE AND SAMPLE TUBE

<u>Temperature</u> $^{\circ}\text{C}/^{\circ}\text{K}$	<u>Silica (2m)</u>		<u>316 SS (2m)</u>	
	<u>t(sec)</u>	<u><math>t^{-1}(\text{hr}^{-1})</math></u>	<u>t(sec)</u>	<u><math>t^{-1}(\text{hr}^{-1})</math></u>
25/298	.469	7676	.475	7579
100/373	.369	9756	.376	9575
200/473	.283	12721	.286	12587
300/573	.223	16143	.228	15789
400/673	.183	19672	.187	19251

$t$  = residence time (seconds)

$t^{-1}$  = space velocity (hours $^{-1}$ )

Table 3-3

## TEST MATRIX FOR EXPERIMENTAL STUDY

<u>Carrier Gas</u>	<u>CO (ppm)</u>	<u>H<sub>2</sub> (%)</u>	<u>HC Species</u>	<u>HC (ppm)</u>
0%	- - - -	- - - -	- - - - -	- - - -
1%	- - - -	- - - -	- - - - -	- - - -
5%	- - - -	- - - -	- - - - -	- - - -
0%	100	- - - -	- - - - -	- - - -
5%	100	- - - -	- - - - -	- - - -
0%	1000	- - - -	- - - - -	- - - -
5%	1000	- - - -	- - - - -	- - - -
0%	2500	- - - -	- - - - -	- - - -
5%	2500	- - - -	- - - - -	- - - -
0%	- - - -	.5	- - - - -	- - - -
0%	- - - -	3	- - - - -	- - - -
0%	- - - -	- - - -	CH <sub>4</sub>	500,1000
5%	- - - -	- - - -	CH <sub>4</sub>	500,1000
0%	- - - -	- - - -	C <sub>2</sub> H <sub>4</sub>	500,1000
5%	- - - -	- - - -	C <sub>2</sub> H <sub>4</sub>	500,1000
0%	- - - -	- - - -	C <sub>3</sub> H <sub>6</sub>	500,1000
5%	- - - -	- - - -	C <sub>3</sub> H <sub>6</sub>	500,1000

Temperature Range: 25-400°C

NO=500 ppm, NO<sub>2</sub>=75 ppm

Sample Tube Materials: 316 Stainless Steel and Silica  
(2 meters long)



measured at Sample Point 1 to assess whether chemical concentration change occurred in the preheat oven. Sample lines leading from points 1, 2, and 3 were short, equidistant, and made of 6.4 mm (0.250 inch) O.D. TFE teflon. Screening tests using varying lengths of TFE teflon were conducted for the current study to assure that  $\text{NO}_2$  absorption was not a significant factor in the present experiment.

Mercury manometers were used to measure and maintain the pressure at each of the three sampling points. The pressures at Sample Points 1, 2, and 3 increased with temperature and were ten percent higher for the silica. The pressures are presented in Table 3-4.

Analysis of  $\text{NO}$  and  $\text{NO}_x$  was conducted with a Beckman Model 951H chemiluminescent oxides of nitrogen analyzer.  $\text{NO}_2$  was determined by the difference between the measured  $\text{NO}_x$  and  $\text{NO}$  concentrations. The (carbon) converter was tested following the procedure outlined in the Federal Register (1974). Hydrogen was measured with a Beckman Model 7C Thermal Conductivity Analyzer. Carbon monoxide and hydrocarbon concentrations were monitored with a Beckman Model 590 nondispersive infrared analyzer. Ammonia and cyanide were measured for a few, select conditions using wet chemical techniques. The doped carrier gas downstream of Sample Point 3 was bubbled through a series of two impingers. The contents of the two impingers were combined, a 100 ml sample was taken and either

Table 3-4  
PRESSURE VS. TEMPERATURE AND SAMPLE TUBE

<u>Sample Tube</u>	<u>Temp. (°C)</u>	<u>P<sub>1</sub> (atm)</u>	<u>P<sub>2</sub> (atm)</u>	<u>P<sub>3</sub> (atm)</u>
Silica	25	1.06	1.03	1.00
	100	1.09	1.04	1.00
	200	1.14	1.07	1.00
	300	1.22	1.11	1.00
	400	1.29	1.15	1.00
Stainless	25	1.04	1.01	1.00
	100	1.06	1.01	1.00
	200	1.10	1.02	1.00
	300	1.14	1.02	1.00
	400	1.19	1.02	1.00

ammonia or cyanide were measured using a specific ion electrode (Orion 95-10 and 94-06 respectively).

The instrumentation employed to measure carbon monoxide, hydrogen, and hydrocarbons was designed to establish and monitor the set point concentrations at Sample Point 2. The sensitivity of the instrumentation was not sufficient to quantitatively evaluate CO, H<sub>2</sub>, and HC concentration changes between Sample Points 1 and 2 and Sample Points 2 and 3. The subsequent discussions in the results section relating to observed changes in CO, H<sub>2</sub>, and HC are qualitative and conjective.

## Chapter 4

### RESULTS

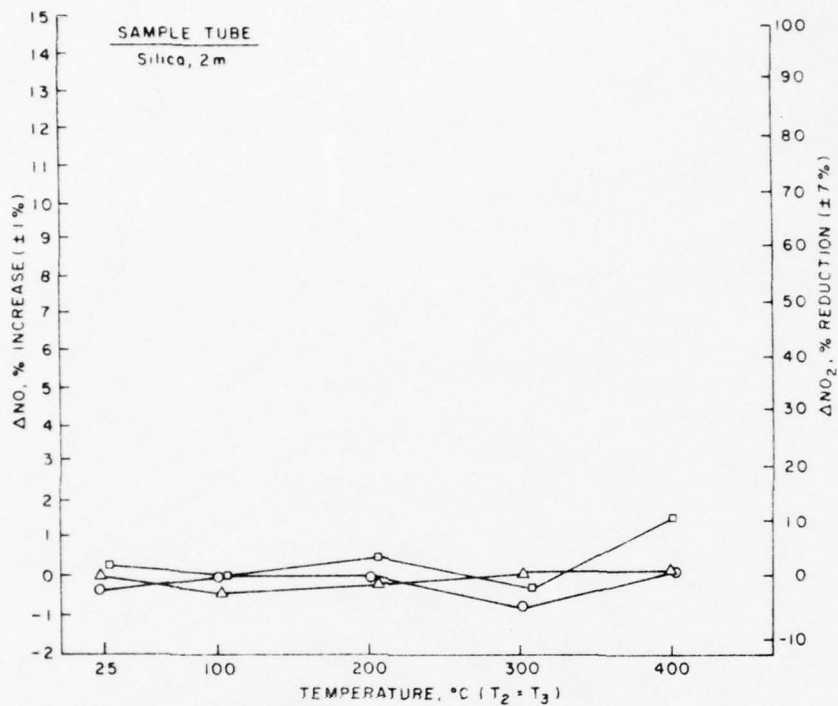
The results are presented in Figure 4-1 for oxidizing mixtures. Results for mixtures with carbon monoxide are presented in Figure 4-2. Results for mixtures with hydrogen are presented in Figure 4-3. Results for mixtures with hydrocarbons are presented in Figures 4-4, 4-5, and 4-6. The percent change of NO and NO<sub>2</sub> represents the percent change in concentration between Sample Points 2 and 3 unless otherwise noted. In the figures, points above the horizontal temperature scale identify those cases for which total NO<sub>x</sub> is conserved. In such cases, changes in nitric oxide (NO) are proportional to changes in nitrogen dioxide (NO<sub>2</sub>) concentration. In those cases for which NO<sub>x</sub> was removed, data are presented in an inset below the horizontal temperature line. The temperature shown is the gas temperature (maintained uniform) at Sample Points 2 and 3.

#### 4.1 OXYGEN MIXTURES

The results for silica are presented in Figure 4-1a. No significant transformation was observed.

The results for stainless steel are presented in Figure 4-1b. In contrast to the results with silica, NO<sub>2</sub> reduction to NO occurred at gas temperatures exceeding 200°C in the absence of oxygen and at temperatures



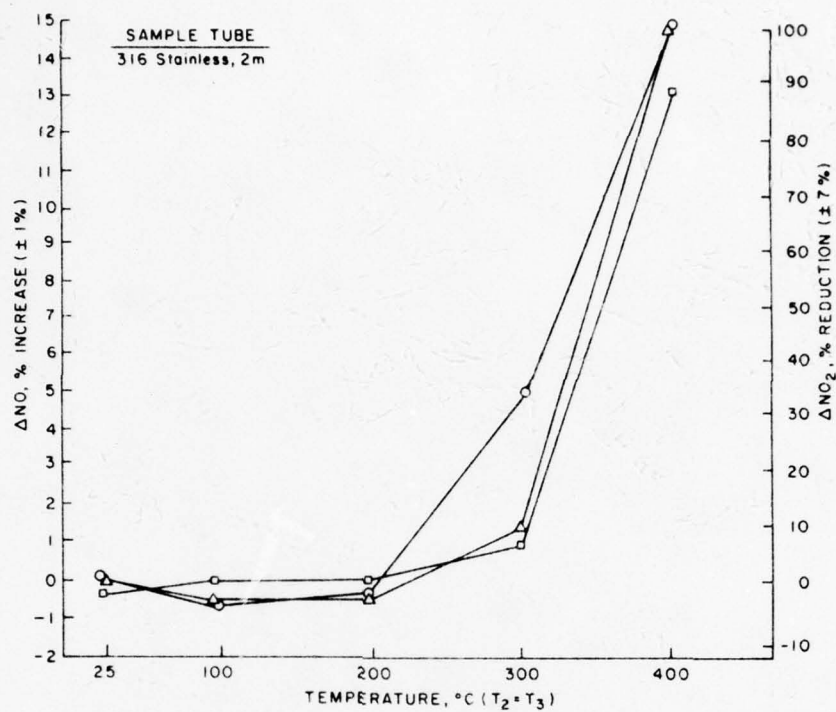


SET POINT CONCENTRATIONS

NO: 500 ppm  
 NO<sub>2</sub>: 75 ppm  
 CO<sub>2</sub>: 12 %  
 O<sub>2</sub>: 0% (O), 1% (Δ), 5% (□)  
 CO: 0  
 H<sub>2</sub>: 0  
 HC: 0  
 N<sub>2</sub>: Balance

FIGURE 4-1 RESULTS WITH OXYGEN

a) Silica Sample Tube



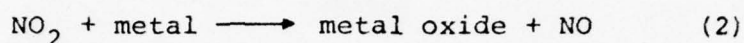
SET POINT CONCENTRATIONS

NO: 500 ppm  
 NO<sub>2</sub>: 75 ppm  
 CO<sub>2</sub>: 12 %  
 O<sub>2</sub>: 0 % (O), 1 % (Δ), 5 % (□)  
 CO: 0  
 H<sub>2</sub>: 0  
 HC: 0  
 N<sub>2</sub>: Balance

FIGURE 4-1 RESULTS WITH OXYGEN

b) 316 SS Sample Tube

exceeding 300°C in the presence of oxygen. The experimental results are consistent with observations by Halstead (1971), Hodgeson et al. (1971), Sigsby et al. (1973), Breitenbach and Shelef (1973), and White and Beddows (1973), and are attributed to the following heterogeneous wall reaction:

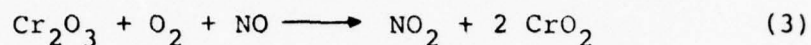


The effectiveness of stainless steel in promoting this reaction likely depends on the condition of the surface layer. Stainless steel is characterized by a thin oxide surface layer. A well prepared and maintained oxide surface will suppress the heterogeneous reaction. However, continued exposure of stainless steel to reducing atmospheres degrades the oxide surface layer and increases the vulnerability of  $\text{NO}_2$  to reduction. The condition of the stainless wall is expected to influence the result and, in fact, such observations have been made in this experiment and others (Tuttle et al., 1973).

For the present experiment, the same off-the-shelf stainless steel sample tube was used under both oxidizing and reducing conditions. The oxide surface layer was not preconditioned or reconditioned for any test run. The presence of  $\text{O}_2$  likely served to protect the integrity of the thin oxide surface layer.

The decreased conversion efficiency of  $\text{NO}_2$  to NO observed with 5%  $\text{O}_2$  at 400°C is attributed to a redox

reaction linked to the chromium content of the stainless steel:



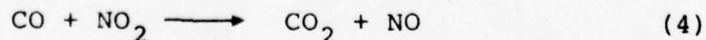
This redox reaction is initiated at or about 400°C and has been identified by Hilliard and Wheeler (1977) as likely responsible for the oxidation of NO to NO<sub>2</sub> at temperatures exceeding 400°C in the presence of stainless steel.

#### 4.2 CARBON MONOXIDE MIXTURES

The results for silica are presented in Figure 4-2a. No significant transformation was observed.

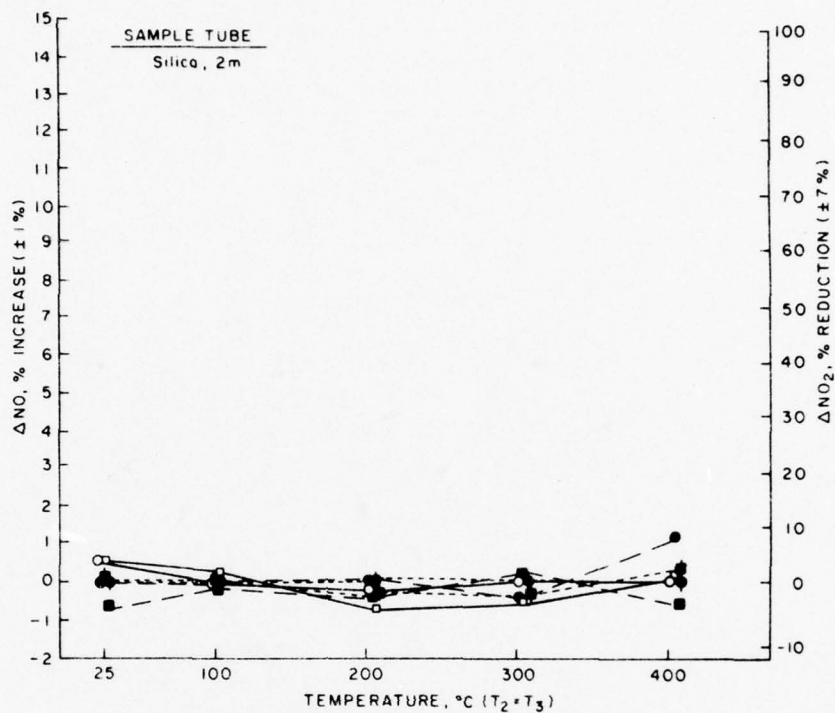
The results for stainless steel are presented in Figure 4-2b. Reduction of NO<sub>2</sub> to NO was observed at temperatures of 100°C and higher. The reduction became more pronounced with increasing CO concentration and increasing temperature. The presence of oxygen suppressed the extent of reduction at a given condition but did not prevent the occurrence of reduction. Note that the results at 100 ppm CO are essentially similar to those obtained in the absence of CO (Figure 4-1b).

The behavior observed in the presence of CO is attributed to the following catalytic reaction:



This observation follows work by others who have addressed the catalytic reduction of NO<sub>2</sub> by CO. For example, Ayen



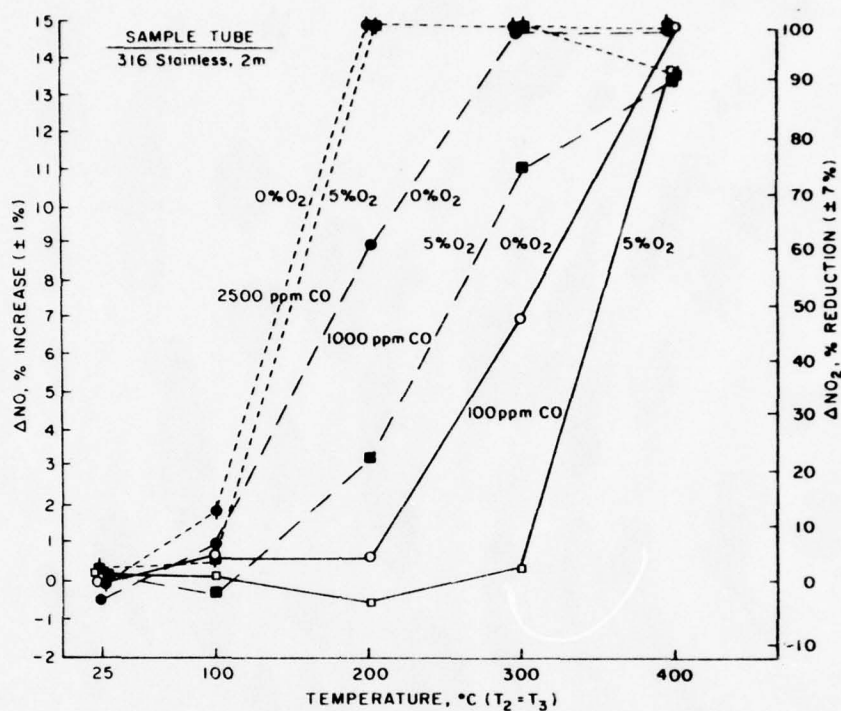


SET POINT CONCENTRATIONS

NO: 500 ppm  
 NO<sub>2</sub>: 75 ppm  
 CO<sub>2</sub>: 12 %  
 O<sub>2</sub>: 0% , 0% , 0% , 5% , 5% , 5%  
 CO: 100 ppm (○), 1000 ppm (●), 2500 ppm (◆); 100 ppm (□), 1000 ppm (■), 2500 ppm (◆)  
 H<sub>2</sub>: 0  
 HC: 0  
 N<sub>2</sub>: Balance

FIGURE 4-2 RESULTS WITH CARBON MONOXIDE

a) Silica Sample Tube



#### SET POINT CONCENTRATIONS

NO: 500 ppm

NO<sub>2</sub>: 75 ppm

CO<sub>2</sub>: 12%

O<sub>2</sub>: 0%, 0%, 0%, 5%, 5%, 5%

CO: 100 ppm (○), 1000 ppm (●), 2500 ppm (⊕); 100 ppm (□), 1000 ppm (■), 2500 ppm (⊗)

H<sub>2</sub>: 0

HC: 0

N<sub>2</sub>: Balance

FIGURE 4-2 RESULTS WITH CARBON MONOXIDE

b) 316 SS Sample Tube

and Yonebayashi (1967) used a barium promoted copper chromite catalyst and observed the reduction of  $\text{NO}_2$  by CO at temperatures of 180-240°C. The reaction products observed were limited to  $\text{CO}_2$  and NO. Similarly, White and Beddows (1973) observed  $\text{NO}_2$  reduction by CO in a 321 stainless steel sampling line.

At 400°C, the effect of oxygen in suppressing the  $\text{NO}_2$  to NO reduction is attributed to the competition between  $\text{NO}_2$  and  $\text{O}_2$  in oxidizing CO. The 5%  $\text{O}_2$  data are independent of CO concentration and converge to the percent reduction observed in the absence of CO (Figure 4-1b). The chromium oxide wall redox reaction (3) is apparently dominant.

#### 4.3 HYDROGEN MIXTURES

The results for silica are presented in Figure 4-3a. No significant transformation was observed up to 200°C in silica with slight reduction (15%) of  $\text{NO}_2$  to NO observed at 300°C. At 400°C, the changes are dramatic and depend on hydrogen concentration.  $\text{NO}_2$  is totally reduced in the silica preheat oven at the lower hydrogen concentration (.5%) with very slight removal of  $\text{NO}_x$  in the silica sample tube.  $\text{NO}_x$  is totally removed in the silica preheat oven at the elevated hydrogen concentration of 3%. The reduction of  $\text{NO}_2$  in silica at 400°C is consistent with results obtained by Ashmore and Levitt (1956, 1957). Complete NO

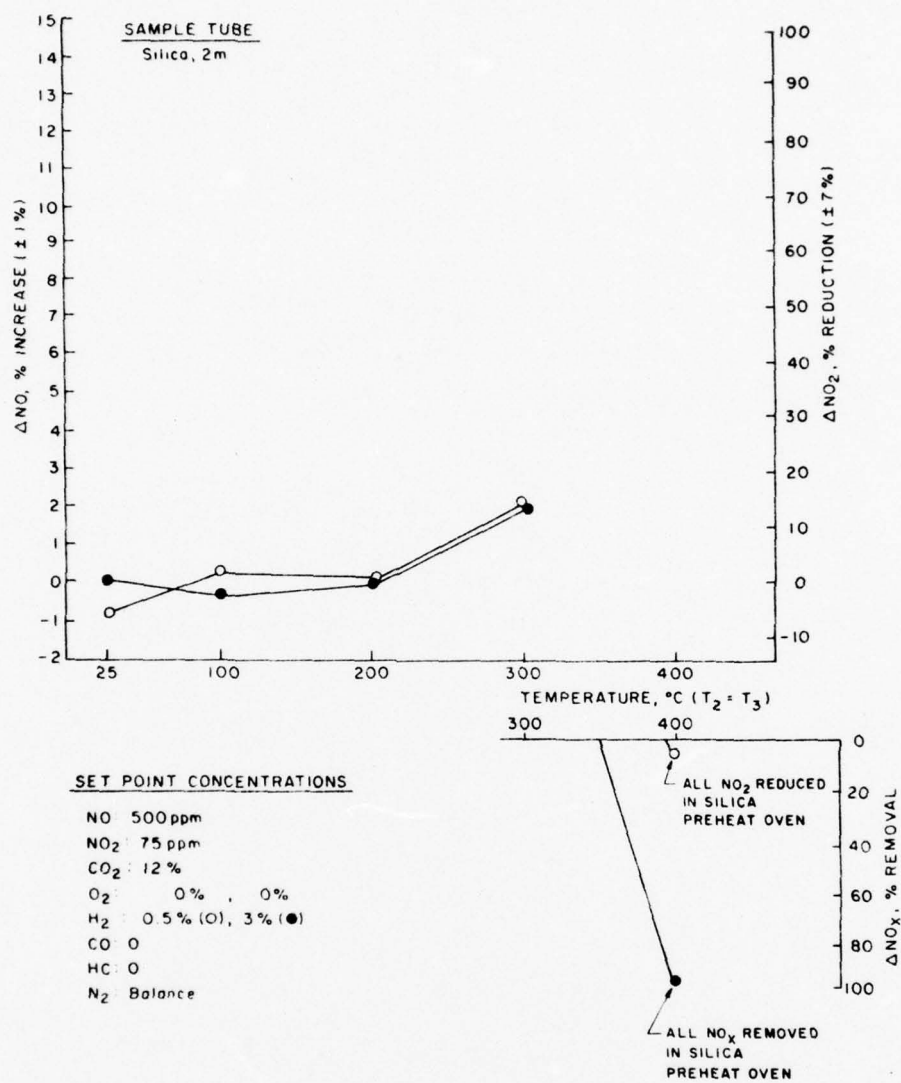


FIGURE 4-3 RESULTS WITH HYDROGEN

a) Silica Sample Tube



reduction by hydrogen may be attributed to (1) the catalytic activity of silica and (2) the elevated concentration of hydrogen.

The results for stainless steel are presented in Figure 4-3b. Complete reduction of  $\text{NO}_2$  to NO was promoted at  $200^\circ\text{C}$  in the presence of hydrogen. At  $300^\circ\text{C}$ , the chemical transformation depended upon hydrogen concentration. Nearly total removal of  $\text{NO}_x$  by .5%  $\text{H}_2$  was observed in the 316 stainless sample tube with no significant change observed in the silica preheat oven. However, all  $\text{NO}_2$  was reduced in the silica preheat oven with 3%  $\text{H}_2$ , and total  $\text{NO}_x$  removal occurred in the sample tube. At  $400^\circ\text{C}$ ,  $\text{NO}_x$  was removed for both hydrogen concentrations. All  $\text{NO}_2$  was reduced in the silica preheat oven for .5%  $\text{H}_2$ , and all  $\text{NO}_x$  was removed in the silica preheat oven for 3%  $\text{H}_2$ . The catalytic reduction of NO in stainless steel is consistent with data collected by Klimisch and Barnes (1972), Shelef and Gandhi (1972) and others using various types of catalytic material.

Formation of carbon monoxide was observed in both the silica preheat oven and stainless steel sample tube. Evidence of CO formation (400 ppm) with 3%  $\text{H}_2$  appeared at Sample Point 3 ( $300^\circ\text{C}$ ) in the stainless steel sample tube. The presence of CO was more significant at Sample Points 2 and 3 while sampling at  $400^\circ\text{C}$ . The concentrations of CO at Sample Point 2 ( $400^\circ\text{C}$ , 3%  $\text{H}_2$ ) for silica and stainless

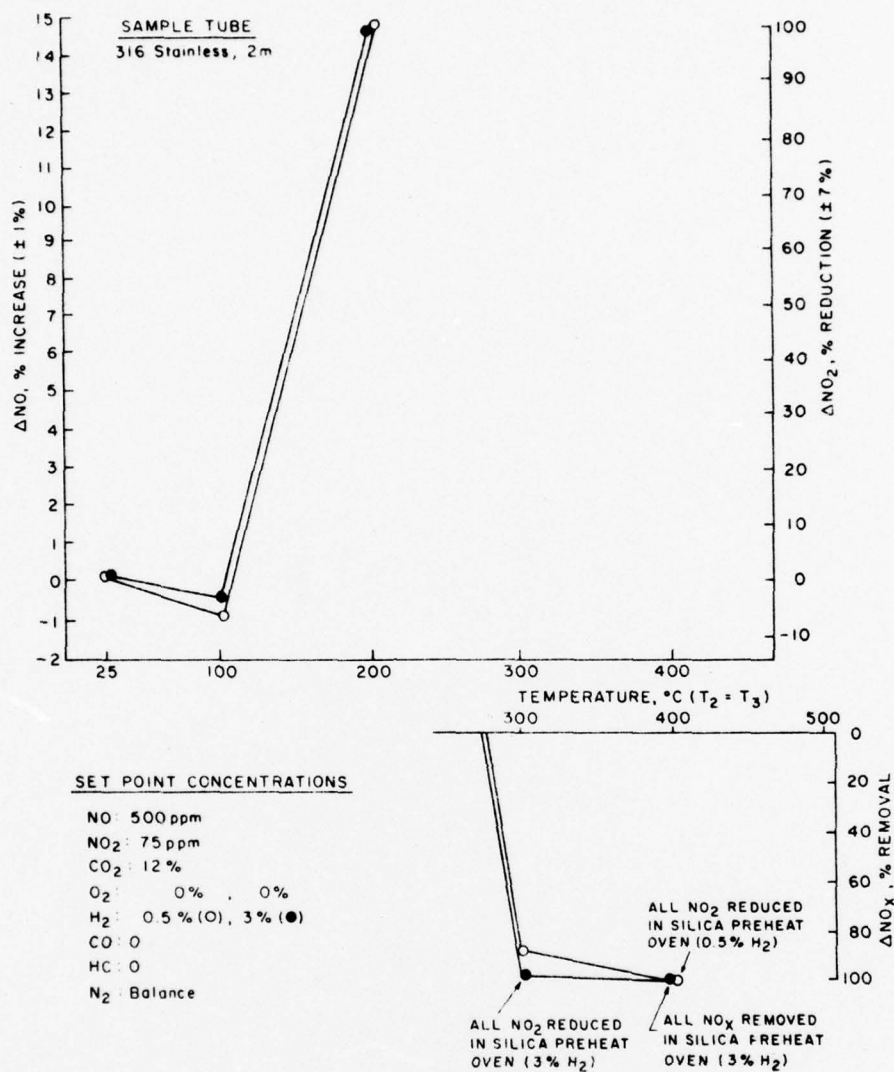


FIGURE 4-3 RESULTS WITH HYDROGEN

b) 316 SS Sample Tube

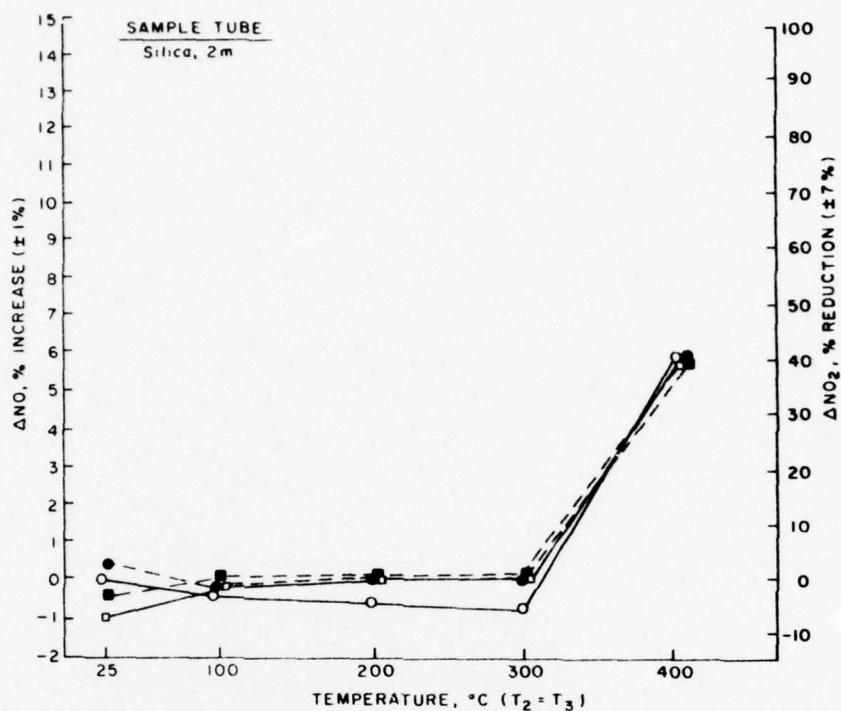
steel tests were 1200 and 900 ppm respectively. The Sample Point 1 concentration of  $H_2$  had to be increased to maintain the desired set point concentration at Sample Point 2. At Sample Point 3, 2800 ppm CO and 3900 ppm CO were formed in the stainless steel tube at  $400^{\circ}C$  with .5%  $H_2$  and 3%  $H_2$  respectively.

The only source of carbon available from the carrier gas mixture for CO formation is  $CO_2$ . A reaction mechanism involving hydrogen and carbon dioxide is proposed for both the silica preheat oven and stainless steel sample tube. The formation of more CO in stainless than silica is attributed to the higher catalytic activity of stainless. Hydrogen will significantly degrade the oxide layer present in stainless and thus increase the catalytic activity to CO formation and  $NO_x$  transformations. Hydrogen also promotes the catalytic activity of silica. However, the presence of CO at Sample Point 2 does not appear to promote either  $NO_2$  reduction or  $NO_x$  removal in silica (Figure 4-2a).

#### 4.4 HYDROCARBON MIXTURES

##### Methane

The results for silica are presented in Figure 4-4a. No significant chemical transformation was observed up to and including  $300^{\circ}C$ . At  $400^{\circ}C$ ,  $NO_2$  to NO reduction occurred. The results were insensitive to the presence of oxygen and the methane concentration.



#### SET POINT CONCENTRATIONS

NO: 500 ppm

NO<sub>2</sub>: 75 ppm

CO<sub>2</sub>: 12%

O<sub>2</sub>: 0% , 0% , 5% , 5%

CH<sub>4</sub>: 500 ppm (○), 1000 ppm (●), 500 ppm (□), 1000 ppm (■)

CO: 0

H<sub>2</sub>: 0

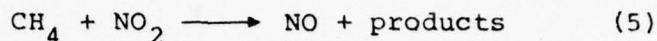
N<sub>2</sub>: Balance

FIGURE 4-4 RESULTS WITH METHANE

a) Silica Sample Tube



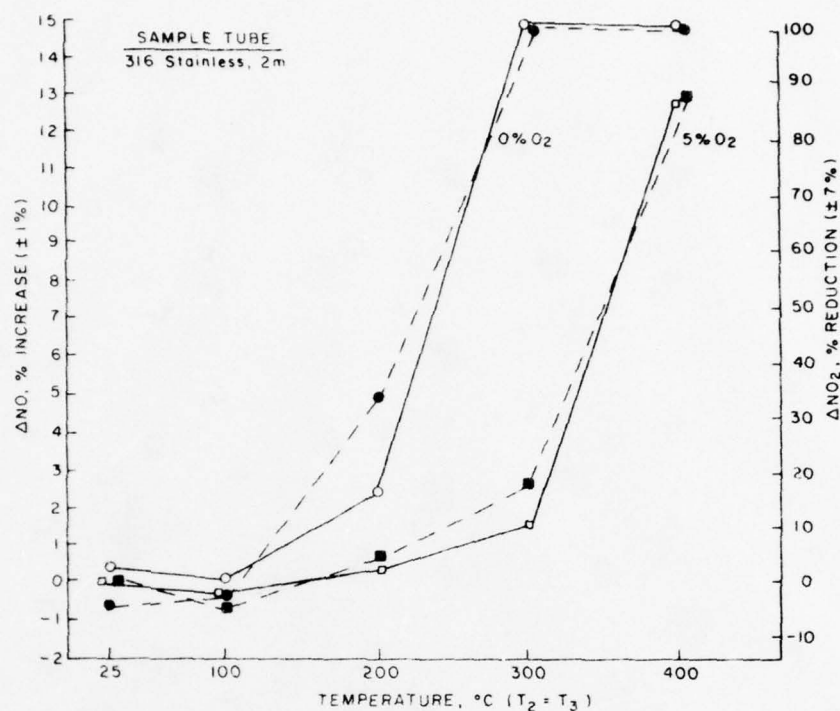
The reduction of  $\text{NO}_2$  to  $\text{NO}$  in silica at  $400^\circ\text{C}$  is attributed to the following homogeneous gas-phase reaction:



This observation is reinforced by the results of studies directed to the gas phase reduction of  $\text{NO}_2$  by methane (Bromberg and Taylor, 1955 and Gagarina and Emanuel, 1959).

The results for stainless steel are presented in Figure 4-4b.  $\text{NO}_2$  reduction is promoted at temperatures exceeding  $100^\circ\text{C}$  in the absence of oxygen and  $200^\circ\text{C}$  in the presence of oxygen. Complete  $\text{NO}_2$  reduction was observed at  $300^\circ\text{C}$  and  $400^\circ\text{C}$  with 0%  $\text{O}_2$  while only 85% reduction was observed at  $400^\circ\text{C}$  and 5%  $\text{O}_2$ . The 5%  $\text{O}_2$  data at  $400^\circ\text{C}$  converged to the percent reduction observed in the absence of reducing species (Figure 4-1b).

Changes in methane and carbon monoxide concentration at  $400^\circ\text{C}$  and at 5%  $\text{O}_2$  within the silica preheat oven and silica and stainless sample tubes are noteworthy.  $\text{CH}_4$  was oxidized by oxygen in addition to  $\text{NO}_2$  in the silica sample tube. Oxidation approached 70%. Some methane oxidation also occurred in the silica preheat oven and the Sample Point 1 concentration had to be increased to attain the set point concentration at Sample Point 2. Although the dimensions of the preheat oven are identical to the silica sample tube, the methane oxidation in the preheat oven was small by comparison because of the thermal gradient



SET POINT CONCENTRATIONS

NO: 500ppm

NO<sub>2</sub>: 75ppm

CO<sub>2</sub>: 12%

O<sub>2</sub>: 0% , 0% , 5% , 5%

CH<sub>4</sub>: 500ppm (○), 1000ppm (●), 500ppm (○), 1000ppm (■)

CO: 0

H<sub>2</sub>: 0

N<sub>2</sub>: Balance

FIGURE 4-4 RESULTS WITH METHANE

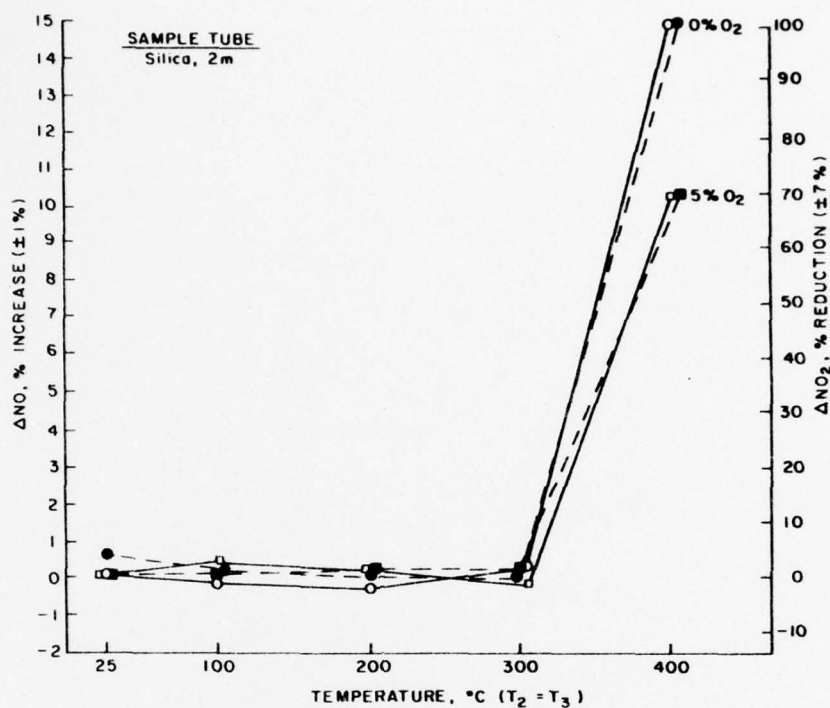
b) 316 SS Sample Tube

from ambient to 400°C. Nevertheless, the methane oxidation by O<sub>2</sub> and NO<sub>2</sub> produced CO. The CO concentration at Sample Point 2 was approximately 100 ppm. At Sample Point 3, the CO concentrations were 400 ppm and 800 ppm respectively for the 500 and 1000 ppm CH<sub>4</sub> set point conditions. CO was not observed within the sample tube for the stainless steel tests. The difference is attributed to (1) the lower overall pressure in the stainless (Table 3-4), (2) the competition for O<sub>2</sub> at the stainless wall between the CH<sub>4</sub> and the chromium oxide (reaction 3), and (3) the catalytic activity of the silica at 400°C (Stadnik and Gomoni, 1963) in promoting HC oxidation.

#### Ethylene

The results for silica are presented in Figure 4-5a. Total reduction to NO was observed at 400°C in the absence of oxygen and seventy percent reduction was observed in the presence of 5% oxygen. The ethylene was totally consumed within the sample tube compared to the 70% oxidation for methane in the presence of oxygen, and explains the less than complete reduction of NO<sub>2</sub> to NO in the presence of oxygen.

The results for 316 stainless steel (Figure 4-5b) indicate that NO<sub>2</sub> reduction is promoted at temperatures exceeding 100°C. Complete NO<sub>2</sub> reduction was observed



SET POINT CONCENTRATIONS

NO: 500ppm  
 NO<sub>2</sub>: 75ppm  
 CO<sub>2</sub>: 12 %  
 O<sub>2</sub>: 0% , 0% , 5% , 5%  
 C<sub>2</sub>H<sub>4</sub>: 500ppm (○) , 1000ppm (●) , 500ppm (□) , 1000ppm (■)  
 CO: 0  
 H<sub>2</sub>: 0  
 N<sub>2</sub>: Balance

FIGURE 4-5 RESULTS WITH ETHYLENE

a) Silica Sample Tube

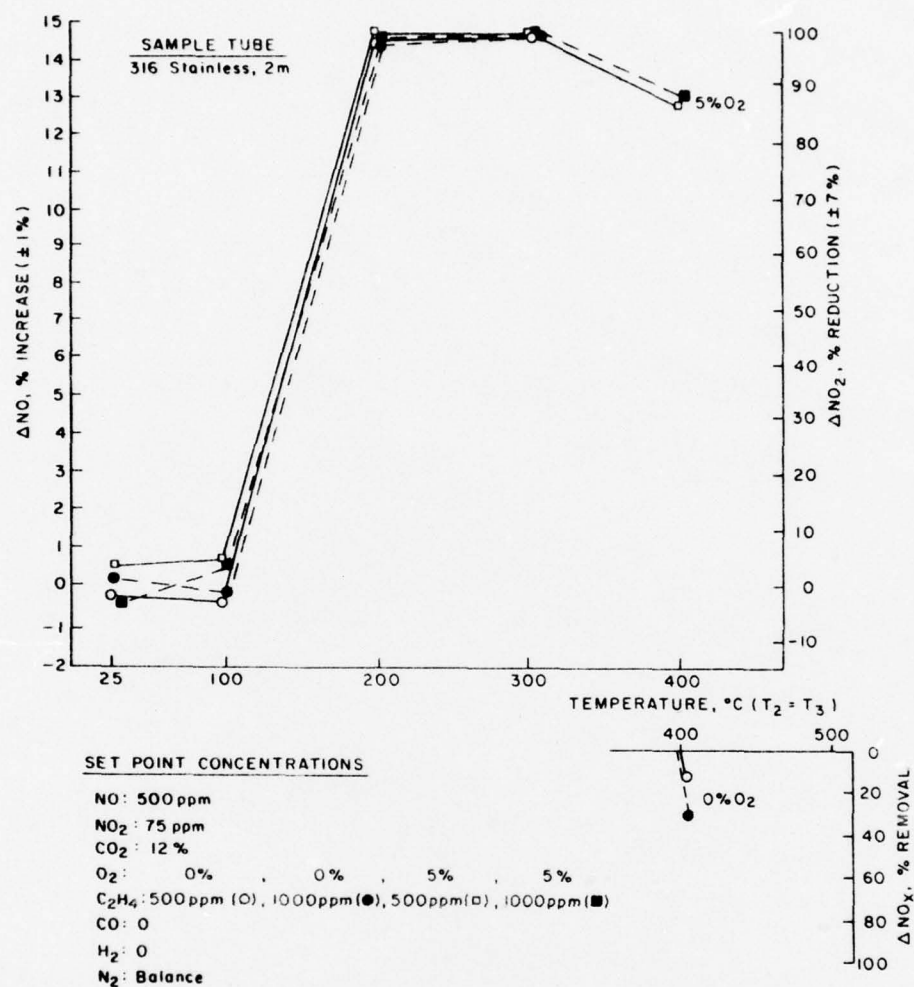


FIGURE 4-5 RESULTS WITH ETHYLENE

b) 316 SS Sample Tube



at 200°C and 300°C with both 0% and 5% O<sub>2</sub>. At 400°C, two types of transformations were observed: NO<sub>2</sub> reduction to NO in the presence of oxygen, and NO removal in the absence of oxygen (the residual NO<sub>x</sub> was composed of NO only). The 5% O<sub>2</sub> data at 400°C once more converged to the percent reduction observed in the absence of reducing species (Figure 4-1b).

The concentrations of CO at Sample Point 2 for both the silica and stainless tests were 1400 ppm and 3000 ppm CO for 500 ppm and 1000 ppm C<sub>2</sub>H<sub>4</sub> respectively as a result of ethylene oxidation in the silica preheat oven. The ethylene flowrate was adjusted to maintain the set point sample tube inlet concentrations at Sample Point 2.

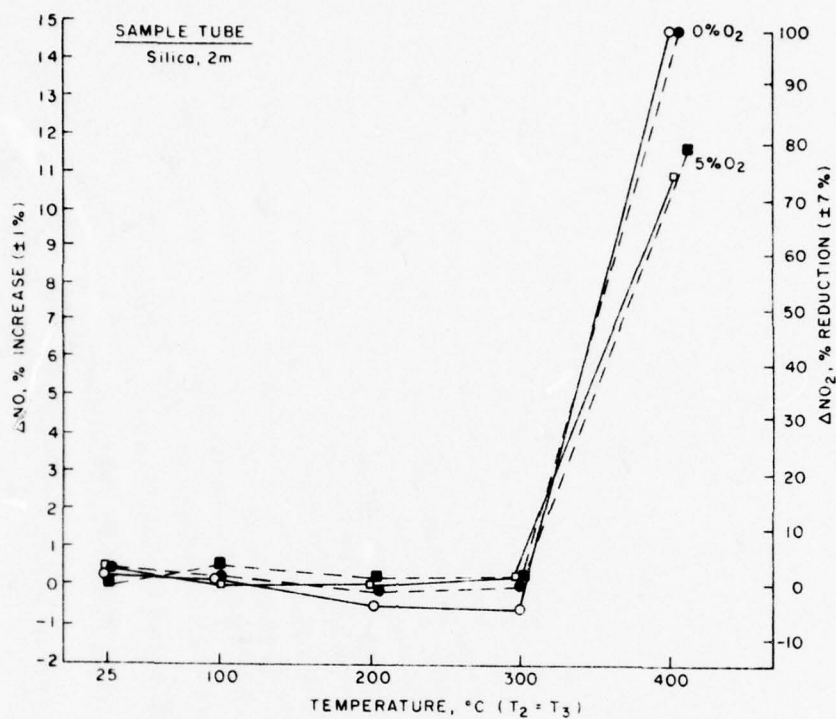
Also notable were the observed differences in ethylene and carbon monoxide concentration change in the silica and stainless steel sample tubes. The consumption of ethylene in the silica sample tube was complete whereas in the 316SS sample tube conversion was approximately 80% for both ethylene inlet concentrations. The difference is attributed to (1) the higher pressure in the silica tests (Table 3-4), (2) the competition for O<sub>2</sub> at the stainless wall between the ethylene and the chromium oxide (reaction 3), and (3) the catalytic activity of the silica. In addition to the difference in hydrocarbon consumption,

a net increase in carbon monoxide concentration was observed across the silica sample tube, whereas a net decrease in carbon monoxide concentration was observed across the stainless steel sample tube. This is attributed to the longer path to  $\text{CO}_2$  in the presence of silica in contrast to  $\text{CO}_2$  yield in the presence of metal or metal oxides (Stadnik and Gomonai, 1963).

### Propylene

The results for propylene are presented in Figure 4-6. The data are basically identical to those with  $\text{C}_2\text{H}_4$  with one significant exception:  $\text{NO}_x$  removal. Propylene is more reactive in the removal of  $\text{NO}_x$ . In the absence of oxygen, slight removal is observed at  $300^\circ\text{C}$  and total removal is observed at  $400^\circ\text{C}$ . Note the consistency of the data at  $400^\circ\text{C}$ , 5%  $\text{O}_2$  with the results in the absence of reducing species (Figure 4-1b).

The higher reactivity displayed by ethylene and propylene with  $\text{NO}_x$  is supported by intuition and reports (Shelef and Gandhi, 1974 and Germain, 1969) that olefins (such as propylene) react more readily with NO than paraffins (such as propane) to form ammonia and/or HCN in the temperature range ( $420^\circ\text{C}$ - $500^\circ\text{C}$ ) for a variety of catalysts. Parenthetically, a brief test was conducted in the present study to determine whether ammonia or HCN were present for the most reactive condition (propylene at  $400^\circ\text{C}$  in stainless steel in the absence of oxygen). Specific ion electrode



SET POINT CONCENTRATIONS

$NO$ : 500 ppm

$NO_2$ : 75 ppm

$CO_2$ : 12%

$O_2$ : 0%, 0%, 5%, 5%

$C_3H_6$ : 500 ppm (○), 1000 ppm (●), 500 ppm (□), 1000 ppm (■)

$CO$ : 0

$H_2$ : 0

$N_2$ : Balance

FIGURE 4-6 RESULTS WITH PROPYLENE

a) Silica Sample Tube

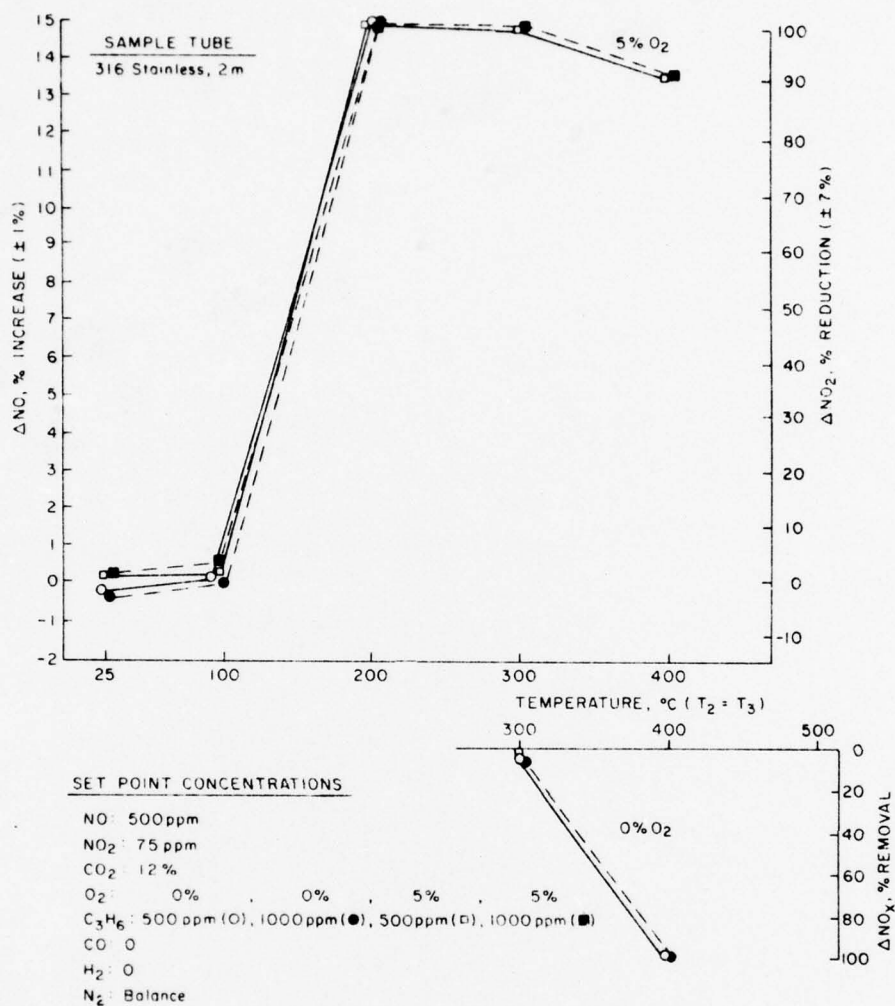


FIGURE 4-6 RESULTS WITH PROPYLENE

b) 316 SS Sample Tube

methods were. The cursory measurement gave no evidence of either species.



## Chapter 5

## SUMMARY AND CONCLUSIONS

## 5.1 SUMMARY

For the sampling conditions associated with the experiment, transformation of nitrogen oxides do occur in the presence of oxidizing and reducing species. Transformations of  $\text{NO}_x$  were more prevalent in reducing mixtures than oxidizing mixtures. The absence of oxygen in the gas stream favored  $\text{NO}_x$  removal by both hydrogen and reactive hydrocarbons. The presence of oxygen in the gas stream prevented  $\text{NO}_x$  removal in both stainless and silica sample tubes. The presence of 5%  $\text{O}_2$  in silica suppressed but did not prevent the reduction of  $\text{NO}_2$  to  $\text{NO}$  with hydrocarbons at  $400^\circ\text{C}$ . With hydrogen,  $\text{NO}_x$  was removed from both stainless and silica. Higher temperatures and pressures were required for the less reactive species such as carbon monoxide and methane to reduce  $\text{NO}_2$  completely in stainless steel. The temperature at which effects were observed, the extent of transformation, and the transformation type depended upon the species present. In particular:

Oxygen and Carbon Monoxide

- $\text{NO}_x$  is conserved in silica and 316 stainless for the temperature range  $25\text{--}400^\circ\text{C}$  in the presence of oxygen and carbon monoxide.

- o Reduction of  $\text{NO}_2$  in 316 stainless steel tubes is observed at temperatures exceeding  $200^\circ\text{C}$ . When carbon monoxide is present, reduction of  $\text{NO}_2$  occurs at temperatures exceeding  $100^\circ\text{C}$ .
- o In silica probes, no significant transformation of nitrogen oxides in the the absence or presence of carbon monoxide is observed.

#### Hydrogen

- o  $\text{NO}_x$  is conserved in silica and 316 stainless sample tubes for the temperature range  $25\text{-}200^\circ\text{C}$  in the presence of hydrogen.
- o  $\text{NO}_2$  is reduced to NO in 316 stainless steel at temperatures exceeding  $100^\circ\text{C}$  in the presence of hydrogen.
- o  $\text{NO}_x$  is removed in 316 stainless steel tubes at temperatures exceeding  $200^\circ\text{C}$  and silica tubes at temperatures exceeding  $300^\circ\text{C}$  in the presence of hydrogen.

#### Hydrocarbons

- o  $\text{NO}_x$  is conserved in silica and 316 stainless sample tubes for the temperature range of  $25\text{-}200^\circ\text{C}$  in the presence of methane, ethylene, or propylene (500, 1000 ppm).

- o  $\text{NO}_2$  is reduced to NO in silica at temperatures exceeding  $300^\circ\text{C}$  in the presence of methane, ethylene, or propylene.
- o  $\text{NO}_2$  is completely reduced to NO in 316 stainless steel at temperatures exceeding  $100^\circ\text{C}$  in the presence of ethylene and propylene, and at temperatures exceeding  $200^\circ\text{C}$  in the presence of methane.
- o  $\text{NO}_x$  is removed in 316 stainless steel at temperatures exceeding  $200^\circ\text{C}$  in the presence of propylene and  $300^\circ\text{C}$  in the presence of ethylene.
- o The presence of excess oxygen (5%) inhibits total reduction of  $\text{NO}_2$  to NO at  $400^\circ\text{C}$  at in gas streams containing methane, ethylene, and propylene with 316 stainless steel tubes.
- o The presence of excess oxygen (5%) inhibits total reduction of  $\text{NO}_2$  to NO at  $400^\circ\text{C}$  with silica tubes in gas streams containing ethylene and propylene.

## 5.2 CONCLUSIONS

Although the combustion effluents were simulated and controlled under laboratory conditions, the results provide some important information concerning probe and

sampling materials. Silica, as expected, limits but does not prevent  $\text{NO}_x$  transformations.  $\text{NO}_2$  reduction to NO occurs at  $400^\circ\text{C}$  in the presence of methane, ethylene, and propylene and  $\text{NO}_x$  removal occurs in the presence of hydrogen. For the species and species concentrations explored, silica would be acceptable for both oxidizing and reducing environments up to  $300^\circ\text{C}$ .

Based on the experimental conditions, conventional 316 stainless steel material effectively promotes transformations of nitrogen oxides and thus may not be an acceptable probe material in the moderate temperature range.  $\text{NO}_2$  reduction is prevalent in both oxidizing and reducing atmospheres, and  $\text{NO}_x$  removal is prevalent in gas mixtures containing hydrogen and reactive hydrocarbons.  $\text{NO}_x$  transformations in 316 stainless steel can be expected in the moderate temperature range leading to errors involved in monitoring the NO/ $\text{NO}_2$  ratio from the exhaust plane of a combustion source. For the species and species concentrations explored, 316 SS would be acceptable for oxidizing environments up to  $200^\circ\text{C}$  and for reducing environments up to  $100^\circ\text{C}$ .

Stated below are a list of general conclusions drawn from the results for sampling combustion effluents:

- o The NO/ $\text{NO}_2$  ratio can be conserved in environments containing oxygen, carbon monoxide, hydrogen, and hydrocarbons with a silica tube at temperatures below  $300^\circ\text{C}$ .



- o Sampling errors regarding the  $\text{NO}/\text{NO}_2$  ratio can be expected with silica in the presence of methane, ethylene, and propylene and hydrogen at  $400^\circ\text{C}$ , and hydrogen at  $300^\circ\text{C}$ .
- o  $\text{NO}_x$  can be conserved in silica for oxidizing and reducing environments with the exception of hydrogen from  $25^\circ\text{C}$  to  $400^\circ\text{C}$ .
- o Sampling errors regarding the  $\text{NO}/\text{NO}_2$  ratio can be expected with 316 stainless steel in the absence and presence of oxygen at temperatures exceeding  $200^\circ\text{C}$ , and in the presence of carbon monoxide, hydrogen, and hydrocarbons at temperatures exceeding  $100^\circ\text{C}$ .
- o  $\text{NO}_x$  can be conserved in stainless steel for environments containing oxygen, carbon monoxide and methane from  $25$ - $400^\circ\text{C}$ .  $\text{NO}_x$  removal can be expected at  $300^\circ\text{C}$  and  $400^\circ\text{C}$  in the presence of hydrogen and olefins.
- o Additional information is needed to more completely assess the role of sample lines and probes in  $\text{NO}_x$  transformations. Residence time, probe history, surface to volume ratio, pressure (at conditions of sub-atmospheric and atmospheric), higher temperatures ( $400$ - $900^\circ\text{C}$ ), additional hydrocarbon species, particulate matter, and alternative



probe materials must be assessed to more fully understand the complex nature of sampling lines and probes for sampling  $\text{NO}_x$ .

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